1) A student who saw his chemistry professor demonstrate a "chemical" cold pack decided to make his own. He looked up the thermodynamic data of a number of compounds, and came to the conclusion that tetramethylammonium iodide would be a good choice since the heat of solution was +42.2 kJ/mol. He decided that a typical cold pack would be stored at room temperature (about 25°C), and that when cold the pack should reach a temperature of 4°C. He found the molecular weight of tetramethylammonium iodide on the bottle, m.w.= 201, and found in his chemistry text that the density of water is 0.9982 g/cm³, its heat capacity is 4.18 kJ/K/kg and the surface tension is 72.7 mN/m. How many grams of the salt should he add per 100ml of water to make his cold pack work as he designed it? (state any assumptions you feel need to be made)

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$$\begin{cases} \text{Heat released when water} \\ \text{is cooled from 25°C to 4°C} \end{cases} = \begin{array}{l} \text{Heat needed to dissolve} \\ \text{TMA. salt} \end{array}$$

100 ml Water cooled from 25°C to 4°C:

$$q = m_{H_2O} \cdot C_p \cdot \Delta T$$

$$q = \rho_{H_2O} \cdot V_{H_2O} \cdot C_p \cdot \Delta T$$

$$q = 0.9982 \cdot 10^{-3} \frac{g}{cm^3} \cdot 100 \, cm^3 \cdot 4.18 \frac{kJ}{kg \, K} \underbrace{(4°C - 25°C)}_{= -21K}$$

$$\underline{q = -8.762 \, kJ}$$

How many grams of TMA salt (x) can be dissolved when 8.762 kJ of heat is provided by the cooling process of 100 ml Water?

$$-q = \frac{q_{solution}}{MW_{salt}} \cdot x$$

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$$x = \frac{-q}{q_{solution}} \cdot MW_{salt}$$

$$x = \frac{-(-8.762 \, kJ)}{42.2 \, kJ/mol} \cdot 201 \, g/mol$$

$$\underline{x = 41.73 \, g}$$

41.73 g of TMA salt added to 100 ml Water at 25°C will cool the solution to 4°C.

2) A graduate student has synthesized two strands of ribonucleic acid (RNA). The two strands, ① and ②, pair with one another to make a duplex.

① 5' GGAACC 3'
3' CCUUGG 5' ②

a) The initial concentration of each strand is 10^{-4} M. From tables of thermodynamic parameters for nucleic acids she can estimate that $\Delta H°$ is -228 kJ/mol and the $\Delta S°$ is -583 J/mol K for formation of the duplex from the single strands. From these data, find the melting temperature T_m, the temperature at which half of each RNA strand will be in the duplex and half will be separated into single strands. State clearly any assumptions you need to make.

$$① + ② \xrightarrow{\Delta H° \atop \Delta S°} duplex$$
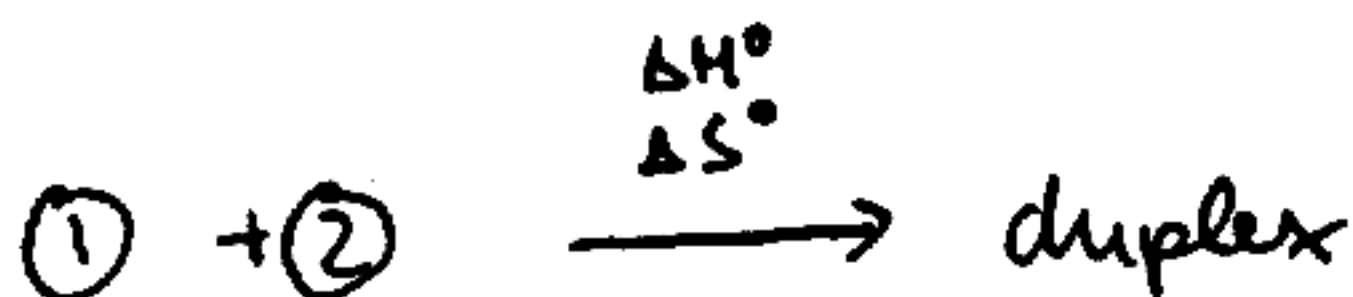
5 $\Biggl\{$ Assumptions: $\Delta H°$, $\Delta S°$ don't change with temperature

5 $\Biggl\{$
$$\Delta G° = \Delta H° - T \Delta S$$

at 25°C:
for duplex formation:

$$\Delta G° = -228 \tfrac{kJ}{mol\,K} - 298\,K\left(-583 \tfrac{J}{K\,mol}\right)$$

$$\Delta G° = -54.27 \tfrac{kJ}{mol}$$

for "melting":
$$\Delta G° = +54.27 \tfrac{kJ}{mol}$$

5 $\Biggl\{$
$$K_{1\,melting} = \frac{[①]\cdot[②]}{[duplex]} = e^{-\Delta G/RT} = e^{\frac{-54.27\,kJ/mol}{8.314\,J/mol\,K \cdot 298K}}$$

$$K_{1\,melting} = 3.074 \cdot 10^{-10}\ M$$

5 $\Biggl\{$
at T_m: 50% of duplex dissociated

$$K_{2\,melting} = \frac{[①]\cdot[②]}{[duplex]} = \frac{0.5\cdot10^{-4}\,M \cdot 0.5\cdot10^{-4}\,M}{0.5\cdot10^{-4}\,M}$$

$$K_{2\,melting} = 0.5\cdot10^{-4}\ M$$

5 $\Biggl\{$
$$\ln\frac{K_2}{K_1} = -\frac{\Delta H°}{R}\left(\frac{1}{T_m} - \frac{1}{T_1}\right) \Rightarrow -\frac{R}{\Delta H°_{melting}} \ln\frac{K_{2\,melting}}{K_{1\,melting}} + \frac{1}{T_1} = \frac{1}{T_m}$$

$$\frac{1}{T_m} = -\frac{8.314\,\tfrac{J}{mol\,K}}{+228\,\tfrac{kJ}{mol}} \cdot \ln\frac{0.5\cdot10^{-4}\,M}{3.074\cdot10^{-10}\,M} + \frac{1}{298K} = 2.918\cdot10^{-3}\tfrac{1}{K}$$

Melting temperature : $T_m = 342.7\ K$

3) Magnesium ions, as well as other divalent metal ions, form important, stable complexes with adenosine triphosphate (ATP) in the cytoplasm. From the text the Mg half cell potential is:

$$Mg^{+2} + 2e^- \rightarrow Mg \text{ is } \varepsilon^° = -2.363 \text{ V}.$$

a) A solution of $Mg^{+2} SO_4^{-2}$ is made at a concentration of 0.01M, with a Mg metal electrode. When this half cell was attached to a H_2/H^+ standard half cell (each at 298 K) the measured voltage was 2.434 V, with the Mg electrode negative. What is the activity of Mg^{+2} in the solution? Does this agree with what you expect? (explain quantitatively).
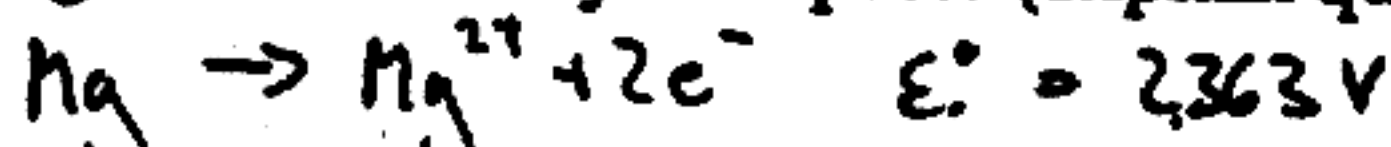
$$Mg \rightarrow Mg^{2+} + 2e^- \qquad \varepsilon^° = 2.363 \text{ V} \qquad \text{Remember: } H_2/H^+ \text{ cell } \varepsilon^° = 0 \text{ V}$$

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$$\Rightarrow \varepsilon \text{ whole cell} = \varepsilon \, Mg/Mg^{2+} \text{ half cell}$$
$$\varepsilon = \varepsilon_0 - \frac{RT}{nF} \ln Q$$
$$2.434 \text{ V} = 2.363 \text{ V} - \frac{8.314 \text{ J/mol·K} \cdot 298 \text{ K}}{2 \cdot 96485 \text{ J/mol·V}} \ln \frac{a_{Mg^{2+}}}{a_{Mg}}$$

5
$$\ln \frac{a_{Mg^{2+}}}{a_{Mg}} = - \frac{2.434 \text{ V} - 2.363 \text{ V}}{8.314 \text{ J/mol·K} \cdot 298 \text{ K}} \cdot 2 \cdot 96485 \text{ J/mol·V} = -5.530$$

With $a_{Mg} = 1$ (solid) $\Rightarrow$ $\underline{a_{Mg^{2+}} = 3.936 \cdot 10^{-3} \text{ M}} \Rightarrow$ With $a = c \cdot \gamma$ $\quad \underline{\gamma_{Mg^{2+}} = 0.3936}$

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$$\log \gamma_\pm = -0.509 |z^- \cdot z^+| \sqrt{I} = -0.509 |2 \cdot 2| \sqrt{0.04} = -0.4072$$

average activity coefficient

$$I = \frac{1}{2} ([Mg^{2+}] \cdot 2^2 + [SO_4^{2-}] \cdot 2^2) = 0.04 \text{ M}$$

$$\Rightarrow \underline{\gamma_\pm = 0.3916}$$ From Debye–Hückel

$\}$ good agreement

b) If the Mg electrode cell is made with 0.001M Mg^{+2}, and then the disodium salt of ATP (Na_2ATP) is added to a total concentration of 0.001M, so that MgATP will be formed. The cell potential (again against a standard H_2/H^+ cell) is measured and is found to be 2.540 V. Find the dissociation constant for MgATP, that is the equilibrium constant for: $MgATP \leftrightharpoons Mg^{+2} + ATP^{-2}$.

The cell voltage is as in a) determined by the activity of Mg^{2+}. The $a_{Mg^{2+}}$ is however reduced drastically by binding of Mg^{2+} by ATP^{2-}: $Mg^{2+} + ATP^{2-} \rightarrow MgATP$

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$$\varepsilon = \varepsilon_0 - \frac{RT}{nF} \ln Q \qquad \text{with } a_{Mg^{2+}} \approx [Mg^{2+}]: \ \varepsilon = \varepsilon_0 - \frac{RT}{nF} \ln [Mg^{2+}]$$

$$2.540 \text{ V} = 2.363 \text{ V} - \frac{RT}{2F} \ln [Mg^{2+}] \qquad \text{Assume } \gamma \approx 1$$
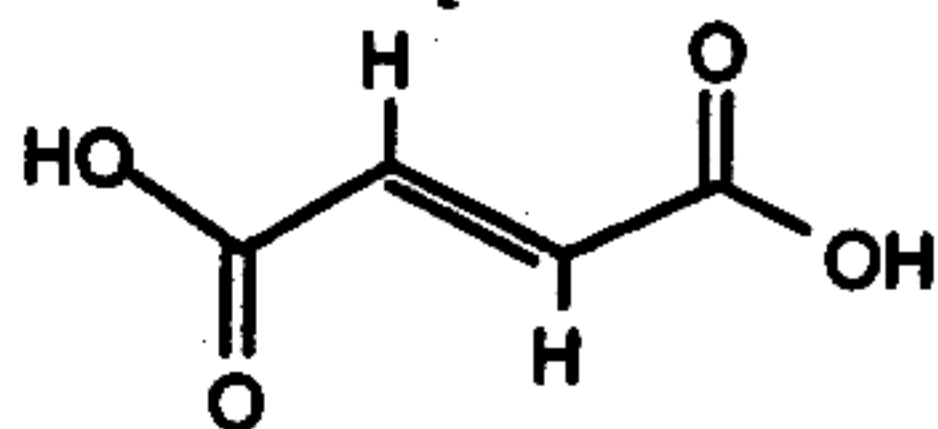
$$\underline{[Mg^{2+}] = 1.030 \cdot 10^{-6} \text{ M}}$$

Dissociation constant for $MgATP \rightarrow Mg^{2+} + ATP^{2-}$

$$K_{Diss.} = \frac{[Mg^{2+}] \cdot [ATP^{2-}]}{[MgATP]} = \frac{1.030 \cdot 10^{-6} \text{ M} \cdot 1.030 \cdot 10^{-6} \text{ M}}{0.001 \text{ M} - 1.03 \cdot 10^{-6} \text{ M}}$$
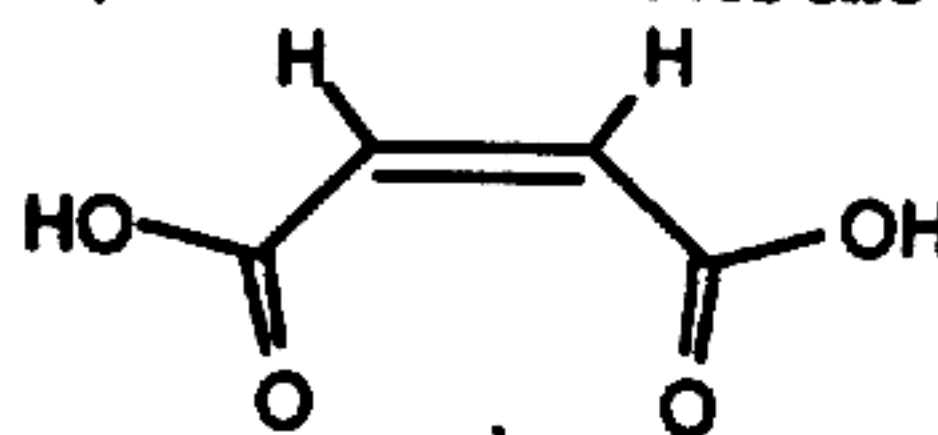
$$\underline{K_{Diss.} = 1.06 \cdot 10^{-9} \text{ M}}$$

4) A student became interested in the relative stability of compounds with *cis* and *trans* double bonds. She found samples of fumeric and maleic acids, with the structures shown below.
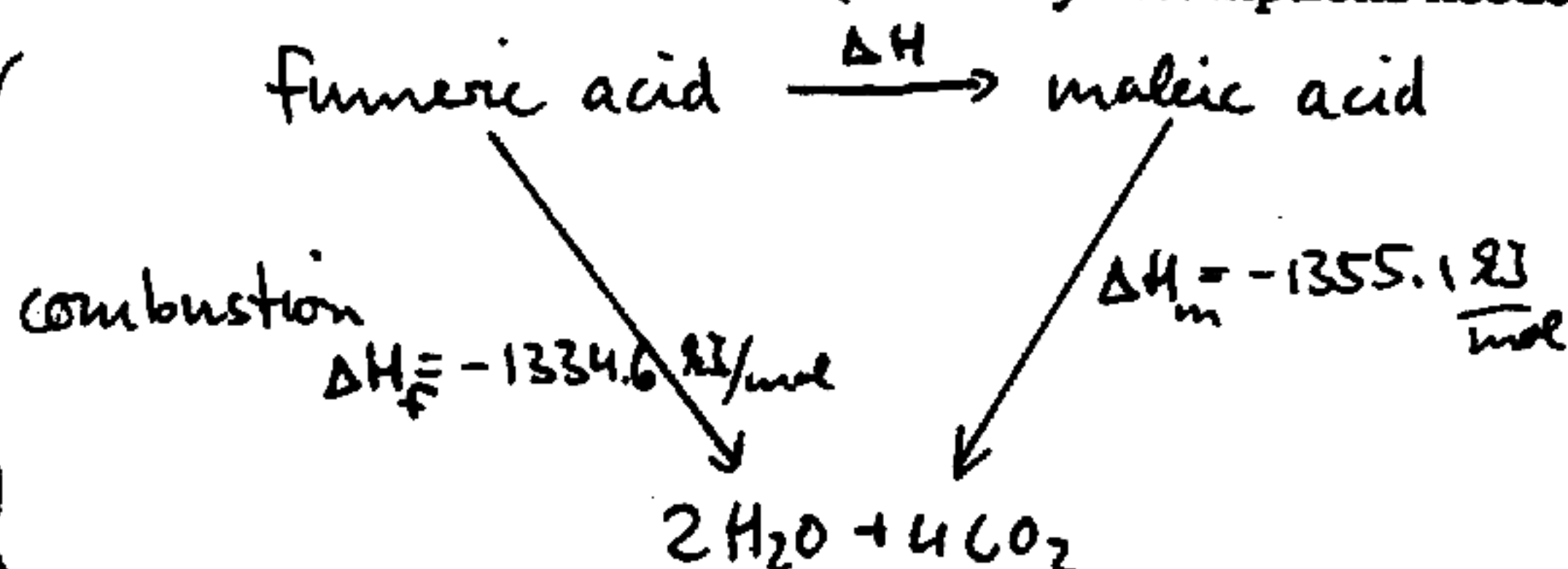

trans
fumeric acid

cis
maleic acid

She did not have much equipment, but did have a bomb calorimeter with which she could measure the heat of combustion of each of these compounds. She burned 1 mole of each in O_2, and found that the heats of combustion were:

fumeric acid $= -1334.6$ kJ/mol and maleic acid $= -1355.1$ kJ/mol.

She also remembered (silly things that stick in your mind) that the heat of formation of CO_2 is -393.5kJ/mol and that of H_2O is -285.8kJ/mol, although she didn't think she needed this information.

a) Should she conclude the double bond stronger in the *trans* compound, fumerate, or the *cis* compound maleate? (State any assumptions needed).

The only difference between the molecules is the cis/trans conformation. The products of combustions are the same $\Rightarrow$ same energies, same ΔS.
ΔS fumeric $\rightarrow$ maleic acid ≈ 0

$$\text{fumeric acid} \xrightarrow{\Delta H} \text{maleic acid}$$

combustion
$\Delta H_F = -1334.6$ kJ/mol

$\Delta H_m = -1355.1$ kJ/mol

$$2 H_2O + 4 CO_2$$

$$\Delta H_{\text{fumeric} \rightarrow \text{maleic}} = \Delta H_F + (-\Delta H_m) = -1344.6 \frac{kJ}{mol} + 1355.1 \frac{kJ}{mol} = +20.5 \frac{kJ}{mol}$$

$\Rightarrow$ Fumeric acid is more stable than maleic acid

$\Rightarrow$ **trans** double bond is stronger than cis double bond.

b) Being a thorough student she also wanted to estimate what the equilibrium constant would be for the isomerization reaction: maleic acid $\leftrightarrow$ fumeric acid.
Although she knew that she was missing some information, she could make a reasonable estimate of the value. Please explain what she had to assume, and what you expect the equilibrium constant to be at 25°C. (hint: this should be very easy to calculate)

Assume $\Delta G \approx \Delta H$ (because same # of molecules: $\Delta S \approx 0$)

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$$K = \frac{[\text{Fumeric acid}]}{[\text{maleic acid}]} = e^{-\Delta G/RT} = e^{-\frac{(-20.5 \text{ kJ/mol})}{8.314 \text{ J/mol·K} \cdot 298K}}$$

$$\underline{\underline{K = 3.923 \cdot 10^3}}$$

$\Delta H_{\text{fumeric} \rightarrow \text{maleic acid}} = +20.5 \frac{kJ}{mol}$

$\Rightarrow \Delta H_{\text{maleic} \rightarrow \text{fumeric acid}} = -20.5 \frac{kJ}{mol}$